BARRIER FUNCTIONS OF SOILS AND SENSITIVITY OF ENVIRONMENT TO POLLUTION

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1. Abstract

The main idea is that chemical processes in soils provide sensitivity and sustainability of ecosystem to pollution. The sustainability to pollution is an inherent property of soil as provided by the system organization of numerous compounds of chemical elements, including pollutants. It has been demonstrated on the base of theoretical and experimental data that this system is capable to create and maintain the own structural-functional system organization in the soil. According to this the species of chemical elements (natural and technogenic genesis) can be divided into firmly tied species that provide the stability of soils (including polluted soils) and available species that provide the buffer ability of soils, the migration of pollutants in landscape and their physiological influence on the living organisms; the last ones are the most important for the environment. The mechanisms of the formation of heavy metals species in the polluted soils have been estimated. It has been proved that the factors that influence on the system of chemical elements in soils have hierarchical organization. Their list is revealed. It has been shown that the theoretical and experimental results can be affective practically used for the rehabilitation of the polluted soils.

2. Introduction

At present time the increasing anthropogenic load on the ecosystem is a real fact, so as the reality of ecological crisis. Chemical pollution is one of main reasons of the dangerous ecological situation. The knowledge of the environmental sensitivity and sustainability limits, as the factors, influencing on it, are very important for the assessment of the modern ecological situation and its forecast. But the theory and methodology of ecosystem sustainability is not fully worked out.

Sustainability of any natural system to any external impact is the inherent system's property, its ability to keep the characteristic structure and functioning. The concept of ecosystem sustainability has vital directionality. Sustainability of ecosystem is realized as the ability of all environmental components to provide and support the vital capacity of living organisms. Sustainability of ecosystem to pollution is one of the types of ecosystem sustainability. It is provided by the ability of all natural media to support the vital capacity of living organisms under pollution.

Ecosystem is the organizing system of all natural media. Soil occupies the central place in this system because of the constant flaws of substances are going throw the soil. All natural media are connected together with forward and reverse communications. As well exposition by aerosol pollution influences on soils, so soil properties provide sufficiently the ecological consequences of their pollution. Natural media has different mechanisms of sustainability to pollution.

The Soils as a special natural component carry out the important functions in ecosystem. They represent a powerful natural biogeochemical barrier, which limits migration of chemical elements in landscape. The most important ecological soils property is their buffer ability as a universal weakening mechanism under the clash of any objects interactions. Two groups of soil properties are important among them: the ability of soils to adsorb chemical elements and to distribute them among the soil components. The most significance has tThe theory of adsorption ability of soil and formation of the system of chemical elements compounds are the main sections in soil science and geochemistry. The present investigation is aimed to investigate mechanisms and to receive the quantitative indexes of metals absorption in noncalcareous soils for the assessment the ability of soils to protect environment from pollution.

3. Objects and methods

Objects of investigation were podzols and soddy-podzolic soils of natural and technogenic landscapes of Russian taiga (Tverskoy, Murmanskiy districts): soil samples, soil extracts, lysimetric water. Methods of investigation (table1) include: 1) determination of the parameters of metals adsorption- desorption (Cu, Zn) by investigated soils in static conditions; 2) fractionating of the species of metals in lysimetric water according to

the charge of their particles, molecular masses, adsorption- desorption on the coal; 3) determination of total metals content and their extractable species by AAS method.

Table 1 The methods of the polluted soils investigation. Laboratory methods

The methods of soil solution receipt	The methods of metal species in soil solution determination	The methods of the mobile forms of metal from the soil solid phases receipt	The methods determination of metals firmly tied species	The methods of the sorption-desorption of metals determination
supplanting by alcohol; - extraction by 0,03-0,05 M $CaCl_2$, $Ca(NO_3)_2$, -vacuum filtration	- ionometric, - division of particles on the ion-exchangeable resins, - division of particles by the electrodialysis -theoretical calculation on the base of thermodynamic constants	-extraction by 1n. CH_3COONH_4	Fractionating metals species from soil	- static, - dynamic

«In situ» methods: ionomethric, lysimetric percolate collection and their analysis, the analysis of the samples from different horizons.

4. Results

The theoretical summarising and experimental investigations show that there are two main groups of metals species in soils: available and firmly tied. Metals in structure of primary and secondary minerals and organic matter present the firmly tied species. Their formation is responsible for the stability of soil towards heavy metals pollution. The mobile (available) species of chemical elements are the most important in view of environment protection. High concentration of these species of heavy metals exerts the ecotoxicological influence. The mobile species in their own turn are represented by two following groups, having actual mobility in soil solution and compounds of solid phases, considered as potentially mobile ones (2). The named two types of compounds are found in dynamic equilibrium. This equilibrium between mobile compounds both in solid phases and in the soil solution provide buffer ability of soil to heavy metals influence. It is realized as the ability of the system of chemical elements compounds to support chemical elements concentration in soil solution. Stability (inertia) and buffer ability (elasticity) of the system of chemical elements species present two types of sustainability of soils towards external chemical load, including heavy metals pollution.

The heterogeneity of soils provides the diversity of the mechanisms of pollutants fixation with soil compounds. K.K.Gedroiz has conceptually established the list of processes, connecting them, 85 years ago. It includes processes adsorption-desorption, precipitation- dissolution and ion exchange. The significance of complexes formation has been established on the last decades.

These processes take place in the conditions of local dynamic equilibrium in soil horizon, soil morphon. But in real soil profile, landscape, biosphere this equilibrium is breached by the flows of substances from without. The processes that influence on the formation and functionering of the system of chemical elements in soil have hierarchical organization. These processes are mating: their forward or reverse flow depends on different factors that are specific for each level of environment, hierarchically organized (table 2).

Table 2 Mechanisms of ecosystem sustainability (stress-bearing capacity) to contamination by heavy metals

Parameters of structural- functional organization of the system of chemical elements in soils at different levels of biosphere organization				Methods of estimation sustainability of the system of chemical elements in soil	Tool to the improvement of polluted ecosystem
Level of the system	Location	Reciprocally bounded components (subsystems)	Mechanisms of sustainability of the system of chemical elements in soil		
Substantial-phase level	Morphon, horizon	Firmly tied substance, available species of chemical elements in the solid phases and in soil solution, soil air, soil biota	Equlibrium processes in heterogenous soil system: sorption-desorption, precipitation-dissolution, ion exchange, complexes. Firm fixation of metals by soil components.	Experimental determination of heavy metals species in soils, sorption capacity and the strength of sorption pollutants by using laboratory modeling and field experiments	Limitation of pollutants availability in soils by applying of adsorbents
Soil-profile level	Soil profile	Soil horizons	Above named processes are accompanied with the biotic flow of substances ups and their water flow down along soil profile	Discovery of the depositary of the pollutants in the soil profile and the quantity assessment of accumulation and migration of pollutants in the soil profile	Limitation of the migration of pollutants in soil profile by creating the shredded putting layers of soil, ground, lime
Landscape level	Landscape	Components of landscape, elemental landscapes	Above named processes are accompanied with the turnover of substance throw the components of landscapes	Discovery of the depositary of the pollutants in landscape and the quantity assessment of accumulation and migration of pollutants in the landscape	Limitation of the migration of pollutants in landscape by planting of grass and trees, which can accumulate the pollutants
Biosphere level	Biosphere	Components of biosphere	Above named processes are accompanied with dilution, transportation of pollutants by air and accumulation in components of biosphere.	Discovery of the depositary of the pollutants in biosphere and the quantity assessment of accumulation and migration of pollutants in the biosphere	There is nothing, except the limitation of pollutants input to biosphere

The elemental level of organization of the system of chemical elements in soils is substantial-phase level. The quantitative parameters of potential affectivity processes of this level have been received in the

laboratory experiments. Their results testifies about participation and significance of all processes (sorption-desorption, precipitation-dissolution, ion exchange, complexes formation) in the formation of the system of chemical elements in different horizons of podzols and soddy- podzolic taiga soils and their sustainability to pollution with heavy metals.

The great attention was focused on the litter horizons of these soils because forests dominate on the territory of Russia. Besides, these horizons are the first that accept the metals of aerosols emissions, dominating in the technogenic regions. The leading position in metals bounding in the letters of the investigated soils occupied presumably the formation of solid Zn salts with organic anions (oxalates, for example). The experimental data indirect confirm it. The lift of Zn concentration in the initial acetic salt solutions, which have been contacted with solutions, containing different concentration of added Zn- ions was not accompanied with the change of Zn concentration in the equilibrium solutions. Such situation can take place in the saturated salt solutions. The same show the results of sorption-desorbtion experiments. The adsorbed Zn-ions were able for the partial desorbtion from the litter.

Humus-accumulative horizon is able to adsorb the most quantity of the added Zn, and it was bounded it predominantly in the exchangeable state. Less than half of adsorbed Zn can be extracted from the polluted soils by weak salt solutions.

The illuvial horizon, enriched with ferri oxides and hydro oxides adsorbed less quantity of Zn ions, but they has been firmly bound specifically, their ability to ion exchange was limited.

Prof. Blum W.E.H. (2007) has marked five parameters for filtering buffering and transformation ability of soil, providing their ecological functions: 1) total inner surface of the soil, 2) constitution of the surface of the components of solid phases,, their specific structure and electrical charge, 3) soil organisms, 4) pH and redox potential of the soil (soil solution), 5) soil temperature.

The potential buffer ability of soils towards heavy metals can be measured with different relative parameters of metals distribution between solution and solid phases: a) ratio of Me concentration in the initial and equilibrium solutions (Cin/C eq) ratio of increase of adsorbed by solid phases metals to the increase of Me concentration in the equilibrium solution ($\partial S/\partial C$), c) ratio of the supply of available Me species in the solid phases to the Me concentration in the soil solution (∂Me available/ CMe solution). The most level of soil buffer ability towards metals was marked in humic horizon. With the increasing of metals load the soil buffer ability has decreased.

The species of metals in the liquid phase of soils is very important for the Me adsorption. The results of electro dialysis of lysimetric water has shown that the metals are presented predominantly by the species with negative or neutral charge This circumstance prevents their adsorption by soil components and increases their mobility. The depletion by metals of the podzol litter is favored with flushing water regime of taiga landscapes. In the polluted soils the entering of metals prevail under their leaching. The results are the follows: the enrichment of litter with metals and high migration of the metals throw the profile of the polluted soils.

5. Conclusion

1. The ability of soil to adsorb heavy metals and distribute them between soils components is the base of defense of ecosystem from pollution. The different processes of substance moving in soils (according to the level of organization of chemical elements species system in ecosystem) provide the differentiation of biogeochemical barriers in soils.
2. The sustainability of soil to heavy metals pollution is provided by their stability (firm fixation by soil components), and by buffer ability (ability to keep the metals concentration in soil solution).
3. Buffer ability of soils towards heavy metals is provided with all mechanisms of metals fixation, their relative participation depends on the special properties of each soils horizon.
4. Methods for the rehabilitation of the polluted with heavy metals soils should be chosen on the base of the sustainability mechanisms of soils to heavy metals pollution.

6. References

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